Studies on the Rate of Reaction of CH and CO. (II) : The Reaction of H and CO

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As the limiting case, we get

$$\frac{dx}{dt}=\frac{(A_2-(x_2)_0)^2\,K_1p}{\{1+(A_2-(x_2)_0)\,K_1pt\}^2} \qquad (6)$$

which has an implicit expression as to x. Putting $(A_2-(x_2)_0)\,K_1p=\alpha$ and $(A_2-(x_2)_0)=\beta^2$, we can rewrite the equation (6) as,

$$\beta\left(\frac{dx}{dt}\right)^{-1/2}=1+\alpha t \qquad (7)$$

which corresponds to the linear relationship between $\left(\frac{dx}{dt}\right)^{-1/2}$ and t. This relation was verified on the results of the authors for the adsorption of H_2 on Ni [2] and [3] Cu, carried by kieselguhr respectively, and those of Soller and others [4]. The test of the equation showed that it was correct for the results observed under comparatively low pressure, e. g. 1/50 atms, pressure. The equation, however, was found not to hold under higher pressures.

This might be probably of the dependence of each elementary process or so remarkable inter-actions between the processes (1) and (2) that can not be neglected.

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22. Studies on the Rate of Reaction of CH_4 and CO_2. (II)

The Reaction of H_2 and CO_2.

Kimio Tarama, Syuichi Hayakawa, Hiroshi Ichikawa and *Shinji Funakoshi.*

The rate of reaction of CO_2 and H_2, one of the reactions which might occur in the thermal reaction of CH_4 and CO_2, was measured by the flow method under the atm. pressure. Under the condition of the reaction temp. 1210–1131°K and the contact time 0.1–1.0 sec., the effects on the degree of conversion in compliance with the alteration of ratio of CO_2/H_2 were observed and the following results were obtained.

1. This reaction is heterogeneous because the rate of reaction is accelerated in the reaction vessel when packed with some quartz fragments.

2. Under the constant velocity of total flow, the reaction rate seems to increase according to the increase of CO_2 content, while there is no apparent change in the range of the ratio CO_2/H_2 larger than unity.

3. When the velocity of CO_2 flow is constant, the conversion of CO_2 decreases according to the increase of H_2 quantity, but when the velocity of H_2 flow is constant, the conversion of H_2 increases, though slightly, as CO_2 increases in spite of shortening the contact time.

4. These results are qualitatively explained by the velocity equation which is derived from the assumption that the reaction of H_2 with CO_2 activated by the adsorption on the quartz surface is the rate determining step, and that the CO_2 adsorption is retarded markedly by the adsorptions of H_2O produced.

5. The apparent Arrhenius' activation energy of this reaction is 25 Kcal.

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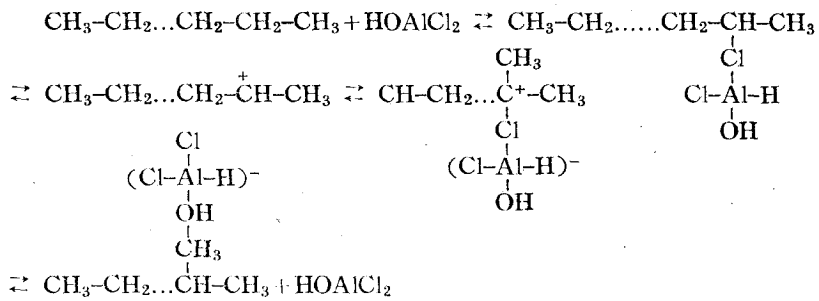
23. Studies on the Catalytic Action of $AlCi_3$.

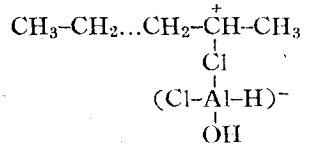
Kimio Tarama and *Toshiaki Kubota.*

To clarify the mechanism of the catalytic isomerization, decomposition and alkylation reactions of n-heptane by $AlCl_3$, the conductivities of catalyst layers were measured. The change of conductivities did not occur under anhydrous condition, but were found to be more remarkable according to the increase of water content in catalyst. The most remarkable change occured under the condition of the mol. ratio of $H_2O/AlCl_3=0.015$, where the catalyst is most active for the isomerization.

From these results, the following mechanism is proposed, i.e. the reaction proceeds through the ionic intermediate complex between heptane and $Al_2Cl_{(6-n)}(OH)_n$, produced from $AlCl_3$ and H_2O, in which n is smaller than 0.5 (simply represented by $OHAlCl_2$).



The fact of progress of decomposition in case of larger water content, is considered that the transfer of H-atom combined with attached to Al in



will be interfered. This supposition might be emphasized by the facts that the decomposition is promoted by the supply of D.S. voltage in the reaction system, and, on the other hand, n-heptane being predominantly decomposed, H-atom disappears in the form of chloroform by the catalyst, mixture of CCl_4 and $AlCl_3$, instead of H_2O.

Finally in case of much more water content, no decomposition occurred probably of the interference of the formation of ionic intermediate complex.